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THE NATIONAL SHIPBUILDING RESEARCH PROGRAM

Contaminated Sediment Management Guide for NSRP Shipyards Appendix 3: Assessment Technologies

U.S. DEPARTMENT OF THE NAVY
CARDEROCK DIVISION,
NAVAL SURFACE WARFARE CENTER

in cooperation with
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DISCLAIMER

SEDIMENT TOXICITY ASSESSMENT

2.1 Introduction

Assessing the toxicity of sediments and any potential threat they pose to human health and the environment is an important step in the remediation process. Presently, several different kinds of tools are available to use in making decisions concerning sediment assessment and desired levels of remediation. Primary tools include environmental regulations and sediment assessment methods; descriptions of their current status form the major sections of this chapter.

2.2 Environmental Regulations that Relate to Contaminated Sediments

Section 121(d) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA), provides that a cleanup must meet the most stringent standard of all the applicable or relevant and appropriate regulations (ARARs), whether that standard originates from another federal environmental law or from a state law. Types of ARARs include:

1. Chemical-specific ARARs - Health or risk-based concentration limits or ranges in various environmental media for specific hazardous substances, pollutants, or contaminants. Chemical-specific ARARs may define protective cleanup levels.

2. Action-specific ARARs - Controls or restrictions on particular kinds of activities related to management of hazardous substances, pollutants, or contaminants. Action-specific ARARs may set controls or restrictions for particular treatment and disposal activities.

3. Location-specific ARARs - Restrictions on activities within specific locations such as flood plains or wetlands.

Sources of ARARs for the remediation of contaminated sediments include international agreements and federal and state statutes and regulations. Major environmental regulations that may apply to sites with contaminated sediments are summarized below. EPA has also published descriptions of these regulations.[1]

2.2.1 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

In addition to the provisions for meeting ARARs mentioned above, the broader objectives of CERCLA are to protect human health and the environment by responding to potential or existing hazardous substance releases, remediating or cleaning up contaminated areas, and assessing liability for remediation actions and resource damages. In general, CERCLA provisions relate either to contamination at abandoned sites where there is a continuing threat of more widespread contamination or to emergency spills. Currently used hazardous sites are generally covered by the Resource Conservation and Recovery Act (RCRA).

CERCLA provides broad authority to locate areas with contaminated sediments. EPA can undertake studies or investigations if it believes a hazardous substance release has occurred or may occur. Studies on the degree and extent of contamination and potential routes of human exposure to a hazardous substance are generally determined through preliminary assessments and may include sampling and testing sediments during site investigations.

2.2.2 Clean Water Act (CWA)

The CWA was designed to restore the physical, chemical, and biological integrity of the nation's navigable waters. There are broad, general requirements under the CWA to locate waters that are not meeting water quality standards and, by extension, waters that have contaminated sediments. The CWA also has specific provisions relating to contaminated sediments: it authorizes the EPA to identify and remove contaminated sediments in harbors and

navigable waterways; to identify contaminated sediments ~~ ~e Chesapeake Bay; to identify contaminated estuar- .n the National Estuary Program (NEP); and to identify and demonstrate remedial options in the Great Lakes. This last provision is being fulfilled under the directions of the Great Lakes National Program Office (GLNPO) as part of the Assessment and Remediation of Contaminated Sediments (ARCS) program. Finally, the CWA authorizes the development of criteria which may apply to dredging and dredged material disposal, assessment, source control, and remediation.

2.2.3 Resource Conservation and Recovery Act (RCRA)

RCRA's overall objectives are to minimize the generation of hazardous waste and to treat, store, and dispose of hazardous wastes so as to minimize present and future threats to human health and the environment. Since one of RCRA's main goals is to prevent the initial release of hazardous wastes into the environment, all treatment, storage, or disposal facilities must meet detailed design, operation, maintenance, and monitoring requirements before receiving an EPA operating or closure permit. RCRA permittees, or applicants for RCRA permits,might have to locate contaminated sediments and RCRA provisions could require a permittee to remediate the sedi- ~~ ts in many circumstances.

2.2.4 Marine Protection, Research, and Sanctuaries Act (MPRSA)

The major purpose of MPRSA is to regulate the dumping of all sewage sludge, industrial waste, and dredged material into the ocean in order to prevent or strictly limit the dumping into ocean waters of any material that would adversely affect human health, welfare, or amenities, or the marine environment, ecological systems, or economic potentialities. The U.S. Army Corps of Engineers (USACE) and EPA have jointly developed protocols to determine if dredged materials can be disposed of in the ocean. These protocols consist of a tiered testing scheme which initially relies on existing information to make a decision on potential contamination. This may be followed by an evaluation of the chemical and physical characteristics of the dredged material and overall environmental conditions at the site. This in turn may be followed by bioassays and bioaccumulation studies to determine whether disposal of the material would result in unacceptable adverse impacts.

2.2.5 Toxic Substances Control Act (TSCA)

~~ \'s objective is to ensure that the manufacturing, processing, distribution, use, and disposal of chemical

substances and mixtures do not present an unreasonable risk of injury to human health or the environment. TSCA applies to the procedure for dealing with contaminated sediments in two ways: first, a contaminant that is commonly found in sediments in excess of sediment criteria may be subject to manufacturing bans, and second, sediments contaminated with greater than 50 ppm PCBs may have to be disposed of by TSCA-approved methods.

2.2.6 Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

FIFRA provisions are similar to TSCA provisions in that the use of a biocide could be restricted nationwide or in certain regions of the country if it commonly exceeded sediment quality criteria. Many of the persistent pesticides have use restrictions under FIFRA and more pesticides may be added to the restricted list.

2.2.7 Clean Air Act (CAA)

The CAA is similar to both FIFRA and RCRA in that emission control provisions would only become important if it could be demonstrated that air emissions were responsible for sediment contamination over wide-spread areas. Alternatively, air emissions from the treatment and disposal of contaminated sediments may have to meet CAA standards.

2.2.8 National Environmental Policy Act (NEPA)

NEPA requires the preparation of an Environmental Impact Statement (EIS) for many federally-funded projects. EIS preparation provides an opportunity to explore the options available for dredging and disposal of contaminated dredged material. NEPA's intent is to incorporate environmental considerations into decision-making at the federal level. National dredging projects are typical of the types of projects that require EISs. NEPA does not provide the legal authority for making decisions, however, and all aspects of control of dredging and dredged material disposal are covered by other environmental statutes.

2.2.9 Rivers and Harbors Act (RHA)

The RHA provides authority for the USACE to carry out projects for the improvement of navigation. It does not authorize dredging for environmental improvement (such as the removal of contaminated sediments). The Water Resources Development Act of 1990 does provide the USACE with some authority to remove contaminated sediments.

2.2.10 Endangered Species Act of 1973

Dredge and fill projects, as well as other activities regarding contaminated sediments, can potentially adversely impact threatened and endangered wildlife species due to habitat degradation or destruction. Thus, such projects fall under the jurisdiction of the Endangered Species Act of 1973.

2.2.11 Great Lakes Water Quality Agreement (GLWQA)

The GLWQA between Canada and the United States is an agreement to restore and enhance water quality in the Great Lakes System. Under the GLWQA, the International Joint Commission Dredging Subcommittee has developed specific sediment classification protocols to assist in determining appropriate disposal options for navigational dredging projects.

2.2.12 State Environmental Statutes that Relate to Contaminated Sediments

Finally, state laws may also apply to contaminated sediments. Examples include state requirements for disposal and transport of radioactive wastes, state approval of water supply system additions or developments, state ground-water withdrawal approvals, state water quality standards, and state air toxics regulations.[2]

2.3 Current Development of Sediment Assessment Tools

Although sediments are an extension of the water column, assessment of sediment toxicity is much more complex than assessment of water quality. Due to the nature of sediment chemistry, presence of contaminants does not necessarily mean that the sediment is toxic. For example, contaminants may be present but chelated with humic material in the sediment and thus unavailable.

This problem has become increasingly apparent in recent years and the EPA is developing a national strategy to address this issue. Under the lead of the Office of Water, the following steps are being taken: (1) review of sediment assessment methods, (2) development of sediment quality criteria, (3) development of the Toxicity Identification Evaluation, and (4) discussion of the need for a consistent, tiered testing approach to sediment quality assessment.

2.3.1 Sediment Methods Classification Compendium

In order to meet a growing concern for establishing a regulatory tool that can be used in the assessment of sites with suspected sediment contamination, a national sediment criteria development effort was undertaken by EPA's Criteria and Standards Division.[3] A Sediment Classification Methods Compendium was developed to serve as a reference for methods that could be used to assess the quality of chemically contaminated sediments.[4] This compendium describes the various methods, as well as their advantages, limitations, and existing applications. These methods are listed and described in Table 2-1.

Each method either directly or indirectly attempts to delimit levels of contamination within sediments such that above those levels either (1) acute and/or chronic toxicological effects become manifest or (2) some amount of bioaccumulation occurs. The sediment quality assessment methods described can be classified into two basic types: numeric or descriptive (see Table 2-1). Numeric methods are chemical-specific and can be used to generate numerical sediment quality values. Descriptive methods are qualitative and cannot be used alone to generate numerical sediment quality values for particular chemicals.

It should be pointed out that the assessment methods in the compendium are not at equal stages of development, and that certain methods (or combinations of methods) are more appropriate for specific management actions than are others. The compendium does not provide guidance on which methods to apply for specific situations or on how different methods can be used as part of a decision-making framework.[4,5]

2.3.2 Sediment Quality Criteria (SQC)

Currently, the EPA is working toward the development of nationally applicable sediment quality criteria. SQC will represent the EPA's best recommendation of sediment contaminant concentrations that will not unacceptably affect benthic organisms or their uses. SQC will be developed separately for each contaminant. At current funding levels, SQC for six non-ionic organic contaminants are scheduled to be developed in FY91, with an additional six to eight criteria documents appearing each year thereafter.

The equilibrium partitioning (EqP) method is the EPA's selected method to establish national SQC. The EqP approach relies on established water quality criteria to assess sediment toxicity. The first basic assumption of the EqP approach is that sediment toxicity is correlated to

Table 2-1. Sediment Quality Assessment Methods[4]

Method	Numeric	Descriptive	Combination	Concept
Bulk Sediment Toxicity	x			Test organisms are exposed to sediments that contain unknown quantities of potentially toxic chemicals. At the end of a specific time period, the response of the test organisms is examined in relation to a specified biological endpoint.
Spiked-Sediment Toxicity	x			Dose-response relationships are established by exposing test organisms to sediments that have been spiked with known amounts of chemicals or mixtures of chemicals.
Interstitial Water Toxicity	x			Toxicity of interstitial water is quantified and identification evaluation procedures are applied to identify and quantify chemical components responsible for sediment toxicity. The procedures are implemented in three phases: 1) characterization of interstitial water toxicity, 2) identification of the suspected toxicants, and 3) confirmation of toxicant identification.
Equilibrium Partitioning	x			A sediment quality value for a given contaminant is determined by calculating the sediment concentration of the contaminant that would correspond to an interstitial water concentration equivalent to the EPA water quality criterion for the contaminant.
Tissue Residue	x			Safe sediment concentrations of specific chemicals are established by determining the sediment chemical concentration that will result in acceptable tissue residues. Methods to derive unacceptable tissue residues are based on chronic water quality criteria and bioconcentration factors, chronic dose response experiments or field correlations, and human health risk levels from the consumption of freshwater fish or seafood.
Freshwater Benthic Community Structure		x		Environmental degradation is measured by evaluating alterations in freshwater benthic community structure.
Marine Benthic Community Structure		x		Environmental degradation is measured by evaluating alterations in marine benthic community structure.
Sediment Quality Triad	x	x	x	Sediment chemical contamination, sediment toxicity, and benthic infauna community structure are measured on the same sediment. Correspondence between sediment chemistry, toxicity, and biological effects is used to determine sediment concentrations that discriminate conditions of minimal, uncertain, and major biological effects.
Apparent Effects Threshold	x		x	An AET is the sediment concentration of a contaminant above which statistically significant biological effects (e.g., amphipod mortality in bioassays, depressions in the abundance of benthic infauna) would always be expected. AET values are empirically derived from paired field data for sediment chemistry and a range of biological effects indicators.

the concentration of the contaminants in the interstitial water and not to the total sediment concentration. The second basic assumption is that contaminants partitioned between the interstitial water and the sediment sorbents (such as organic carbon) are in equilibrium. Therefore, for a given contaminant, if the total sediment concentration, the concentration of sorbent(s), and the partitioning coefficient are known, then the interstitial contaminant concentration can be calculated. The interstitial contaminant concentration can then be compared to established water quality criteria to assess sediment toxicity.[6,7,8]

Due to variation in the specific sediment sorbent(s) that different classes of contaminants sorb to, methodologies for deriving SQC vary with different classes of compounds. For non-ionic organic chemicals the methodology requires normalization to organic carbon. For metal contaminants a methodology is under development and is expected to require normalization to acid volatile sulfide.

2.3.3 Toxicity Identification Evaluation (TIE)

Over the past two years, the National Effluent Toxicity Assessment Center (NETAC) at the Environmental Research Laboratory in Duluth, Minnesota has been developing and publishing guidance concerning methods to identify specific causes of acute toxicity in aqueous samples. These TIE methods, although originally developed for effluents, have been applied successfully to toxic aqueous sediment fractions (pore water, elutriates). The ability to identify compounds responsible for sediment toxicity could prove to be critical to initiating control of their release by point source dischargers and also could be helpful for attributing contamination to specific historical discharges for the purpose of remedial activities.

NETAC's assistance in this project will target high priority sediment toxicity problems, preferably in systems with a limited number of dischargers. In addition to identifying the source of toxicity problems, NETAC's analysis may include recommendations on the methods for solving these problems. These initial cases will also serve as models for conducting sediment TIEs.

2.3.4 Tiered Testing

The development of a consistent tiered testing methodology may provide a uniform basis for EPA decisions regarding the regulation and remediation of contaminated sediments. The need for such a methodology is currently under discussion at EPA. One possible model is the tiered testing scheme used to evaluate the suitability of dredged materials for ocean dumping. This scheme is described in the "Green Book," currently being updated by

the EPA's Office of Marine and Estuarine Protection (OMEP) and the USACE.[9] The testing scheme consists of four tiers:

1. Analysis of existing information and identification of contaminants of concern.

2. Evaluation of sediment and site conditions.

3. Evaluation of acute bioassays and short-term bioaccumulation studies.

4. Evaluation of chronic bioassays and long-term bioaccumulation studies.

Evaluation at successive tiers is based on increasingly extensive and specific information that may be more time-consuming and expensive to generate, but that provides increasingly comprehensive evaluations for environmental effects.

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SEDIMENT SAMPLING SURVEYS

An accurate assessment of the physical, chemical, and biological characteristics of sediments is highly dependent on the collection of representative samples of the sediments. Any sediment samples collected for analysis represent but a small fraction of the total sediments of interest. Careful consideration must therefore be given to ensuring that those samples accurately reflect the characteristics of the sediments in the area they were collected.

In general, contaminants tend to be associated more with fine-grained sediments (e.g., silt or clay) of high organic content than with coarse-grained sediments (e.g., sand or gravel). Fine-grained sediments originate in part from suspended organic particles that adsorb various contaminants from the water column. Once they settle and are buried over time by newer sediments, the original link with contaminant sources and water quality in general may be broken. A recent USEPA document (USEPA 1990) makes this important point:

> It is worth noting that sediment contamination problems need not be connected to poor water quality. The ability of sediments to retain contaminants over time makes it possible for sediments to remain contaminated while water column contaminant concentrations remain below applicable water quality standards.

The distribution of chemical contaminants in sediments depends not only on local contaminant sources, both past and present, but also on natural and anthropogenic processes that redistribute contaminated sediments. In most urban-industrial harbors, like those studied in the ARCS Program, the distribution of chemical contaminants in sediments may be highly variable and "patchy" both horizontally and vertically. In shipping channels, or wherever navigational dredging occurs frequently, contaminated sediment deposits are likely to be relatively thin unless contaminants are mixed to greater depths by vessel propeller scour. However, in areas where dredging was once practiced and then ceased years ago, relatively thick layers of contaminated sediments may have accumulated. Sediment quality in these depositional areas can reflect a complex history of pollution events that have occurred over a span of decades. In this situation, surveys that are limited to collection of a few grab samples of surficial sediment (i.e., a few centimeters) will not produce results that accurately represent the sediment quality. The number, location, and type of sediment samples (e.g., grab samples or sediment cores) must be carefully planned to ensure an accurate assessment of sediment quality.

Field surveys are generally conducted to provide data on sediment contamination that will be used to make decisions on the need for and extent of sediment remediation. The design of field surveys should consider the following factors:

- Historical chemical and physical data on sediments in the area

- The magnitude of currents in the area and their potential effect on sediment accumulation or erosion (i.e., where currents are strong and the area is likely to be erosional; where currents are weak and the area is likely to be depositional; or where the area is susceptible to periodic, high flow events [e.g., floods] that can cause erosion in an otherwise depositional environment)

- The history of dredging in the area

- Bathymetric surveys of the area

- The future need for navigational maintenance dredging or other dredging associated with construction projects.

Historical sediment chemistry data may identify areas likely to require more intensive investigation or chemicals of particular interest. Historical data on physical properties (e.g., grain size) of the sediments may provide an indication of whether a given area is more likely to represent an erosional or a depositional environment.

In erosional environments where bottom sediments generally consist of coarse sand or gravel, there is a lower likelihood of sediment contamination, and sampling by routine methods (e.g., grab samplers or sediment corers) may be precluded.

In depositional environments where there is a very low likelihood of sediment resuspension associated with high flow events or dredging, or where transport of contaminants by groundwater is unlikely, the potential need for sediment remediation can be assessed by sampling only surface sediments. Humans, aquatic organisms, and wildlife will generally only be exposed to sediment contamination in the uppermost "active" layer of the sediment deposit. Unless groundwater transport is significant, release of contaminants to the water column will only occur from the sediments in contact with the water. Hence, contaminated sediments separated from the overlying water by a surface layer of relatively clean sediments may not represent an ongoing risk to humans, aquatic organisms, or wildlife. In such cases, the best remedial alternative may be no action, allowing additional deposition and accumulation of cleaner sediments to further isolate the contaminated sediments.

If surface sediments in a depositional environment are sufficiently contaminated to require evaluation of remedial alternatives, it will then be necessary to sample subsurface sediments as well. This sampling should be designed to provide information that can be used to define the vertical extent of sediments that may need to be dredged, to investigate remedial alternatives for those sediments, and to characterize the sediment that will be left in place and exposed once the overlying contaminated sediments are removed.

It will also be necessary to sample subsurface sediments in areas subject to periodic, high flow events, which can cause erosion in an otherwise depositional environment, as is

often the case in Great Lakes AOCs. The depth to which sampling must extend should be based on an analysis of the likelihood of erosion extending to a given depth during an event of a predictable magnitude.

It is difficult to provide generic guidance on the depth of subsurface sediments that will need to be sampled. Historical dredging records or bathymetric surveys may be used to estimate sediment accumulation rates in a given area, which may in turn be used to estimate the depth of sediments that may have accumulated since some historical event of importance (e.g., the initiation of a specific point-source discharge in the local area). In many cases, it may be necessary to conduct a survey in several phases. If the results of early phases indicate sediment contamination extending to the maximum depths sampled, further sampling will likely be required at greater depths. Often, the depth of sampling is determined by equipment limitations.

In areas subject to navigational maintenance dredging or other planned dredging projects, it will likely be necessary to sample sediments over the entire depth to be dredged. In addition, sediment samples should be collected from just below that depth to characterize the sediment that will be left in place and exposed once the overlying contaminated sediments are removed.

ARCS Program field surveys were designed to conduct representative sampling of thick (up to 6 m deep) deposits of contaminated sediments and to provide data for 3-dimensional mapping of sediment quality. It was considered important to characterize sediments with depth, because contaminant concentrations in surface sediments were sufficiently high that remediation was considered likely to be required. It was therefore necessary to establish the vertical extent of sediment contamination.

This chapter describes procedures for collecting sediment samples for an integrated sediment assessment (including physical, chemical, and biological characterization of the sediments). Topics discussed include the sediment sampling vessel; field positioning methods; sediment sampling procedures; field processing of sediment samples for physical and chemical analyses, benthic community analyses, and toxicity testing; and sediment characterization by remote sensing. As appropriate for each topic, various options or objectives are discussed, the procedures used in the ARCS Program are described, and recommendations are made for procedures to use in future sediment surveys of other Great Lakes AOCs.

SEDIMENT SAMPLING VESSEL

Many types of vessels can be used to sample sediments in Great Lakes AOCs. Several issues that need to be considered when choosing the type of vessel include, but are not limited to:

- Trailerability

- Required lifting capacity (including required buoyancy, balance, and winches)

- Whether sample processing should be conducted on board

- Need for a protective cabin

- Vessel draft (ability to operate in 0.5 m of water)

- Need for precise location, depth, and other electronic equipment.

Sampling Vessel Used in the ARCS Program

A vessel operating in protected waters such as rivers and harbors does not require a design suitable for operation in heavy weather. The boat constructed for the ARCS Program, the R/V *Mudpuppy* (Figure 3-1), is a monohull aluminum barge with an overall length of 30 ft (9.2 m), an 8-ft (2.4-m) beam, and a draft of 1.5 ft (0.5 m). The hull consists of four sealed compartments and is flat-bottomed, with a 5° V-shaped bow and a square foredeck. This design provides the maximum forward buoyancy needed for sample collection. A lifting boom is mounted on the bow, and a recessed cabin is located at the stern. The vessel is powered by twin outboard engines, which are mounted on an extended bracket to minimize loss of deck space. Electrical power for onboard instrumentation and cabin air conditioning is provided by a diesel generator located on the aft deck. Continuous electrical power for the ship's lights, communications, and winches is provided by two 12-volt batteries. Electronic instruments used in vessel operations include a marine radio, a fathometer, a global positioning system (GPS), computers for data logging and navigation, and a Loran-C receiver, which serves as a backup for the ship's positioning system.

A trailerable vessel was considered necessary to provide the most cost-effective means of moving between study sites. Because the R/V *Mudpuppy* has a maximum 8-ft (2.4-m) beam, it meets the maximum allowed trailer width for highways. A greater beam would require trailering as a "wide load," and would require additional safety measures and towing experience.

A work boat's hull needs to be rugged and able to resist the dents and scratches that plague boats working in industrial marine areas, such as Great Lakes AOCs. Wood and fiberglass do not provide the protection from hull damage offered by aluminum or steel. For the R/V *Mudpuppy*, aluminum was chosen as the hull material. Although steel provides more strength, aluminum provides a strong but light vessel that is more easily trailered.

The deck layout confines all sampling activities to the forward 14 × 8-ft (4.3 × 2.4-m) deck, providing the vessel operator with a clear view of all sampling operations. Bow-mounted catwalks fold down forward providing additional work deck around the coring operations. To provide maximum buoyancy and minimum heel, all sediment coring is conducted from the bow using a 13-ft (4-m) long, rectangular lifting boom with a 2,000-lb (900-kg) lift capacity. The bow-mounted boom also allows sediment cores to
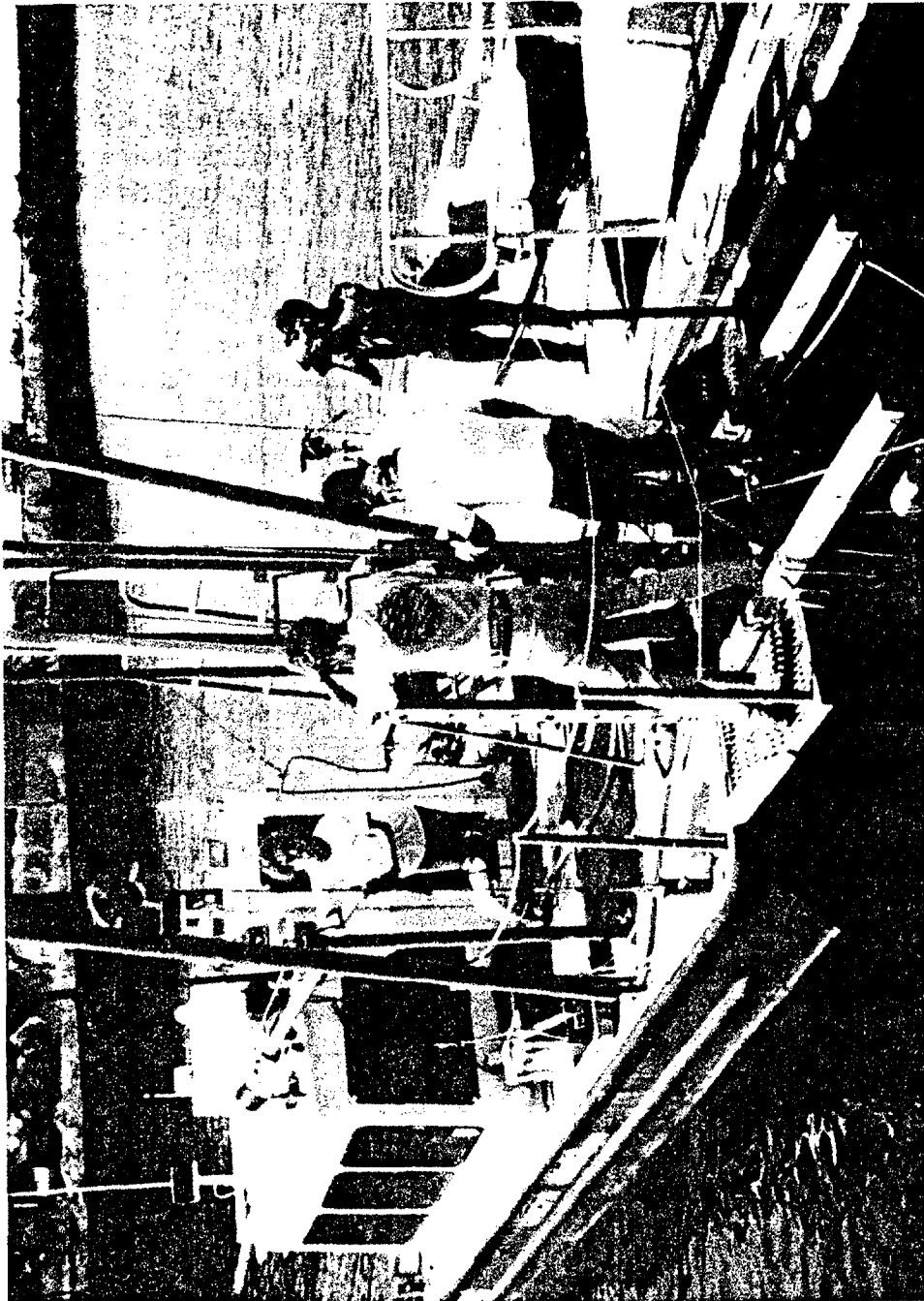
Figure 3-1. R/V *Mudpuppy.*

be collected near the shore or obstructions while preventing possible damage to the engine propellers. Two electric lifting winches, one 110-volt AC and one 12-volt DC, each wound with 0.25-in. (0.64-cm)-diameter, stainless-steel cable, lift the sampling gear and sediment cores (see *Sediment Sampling Procedures*). When the vessel is trailered, the sampling boom is lowered aft over the cabin roof, allowing the total height of the trailered vessel to meet highway height restrictions.

The R/V *Mudpuppy* has worked well, providing a rugged, trailerable, shallow-draft work platform. It is capable of operating in confined areas, providing both a stable platform for sample collection and a climate-controlled cabin for instrumentation.

FIELD POSITIONING METHODS

Accurate positioning of sampling stations is essential for field investigations of sediment characteristics. Because of navigational dredging activities and hydrology in Great Lakes AOCs, contaminated sediments frequently occur in narrow bands along shorelines or in localized pockets. To accurately map such areas, positioning of high accuracy is needed. In addition, contour mapping algorithms depend on accurate measurements of distances between sampled and estimated points. Inaccurately determined sampling locations will introduce mapping error. Often, additional sampling is needed at previously sampled stations, requiring accurate positioning to relocate at the same station.

Although relative positions can be determined by measuring bearings and distances from reference points on shore, absolute positioning is required to link positions to a geographic coordinate system (e.g., latitude/longitude, state plane coordinates).

Requirements for an ideal positioning system are:

- Minimum accuracy of < 1 m

- No required shore access to reference points (to eliminate the need to gain access to privately held industrial property bordering many rivers and harbors)

- Capability for real-time position determination

- Positions output in geographic coordinates (e.g., latitude/longitude) to facilitate conversion to other coordinate systems (e.g., state plane coordinates)

- Minimal operator involvement

- Ability to coordinate position data with other simultaneously collected data (e.g., seismic data)

- Position updating at intervals of no more than 3 seconds

- Ability to log positions for later review and/or processing

■ No interference from waterside structures and natural features

■ No "black out" periods, during which the system does not function

■ Low cost.

Advantages and Disadvantages of Available Positioning Systems

A number of different positioning systems were investigated as part of the ARCS Program. Selected capabilities and features of the various systems are summarized in Table 3-1 and in the subsections that follow.

TABLE 3-1. COMPARISON OF POSITIONING SYSTEMS

	LORAN-C	MICROWAVE	GPS
Absolute accuracy	400 m	3 m	<1–5 m[a]
Repeatable accuracy	10–15 m	3 m	<1–5 m[a]
Shore access required	No	Yes	No
Real-time capability	Yes	Yes	Yes
Frequency of fixes	Continuous	Continuous	Continuous
Cost	Low	High	Medium

[a] Assumes differential global positioning system, and varies with the manufacturer of the receiver.

Loran-C

Loran-C is a land-based radio navigation system that calculates positions based on time differences between master/slave transmitter pairs. Although the cost of Loran-C receivers is low and the repeatable accuracy is good, they have less than acceptable absolute accuracy (0.25 miles or 400 m) and are prone to interference by bridges and other large metal structures commonly found along industrialized rivers and harbors.

Microwave Ranging Systems

Microwave ranging systems calculate positions by determining distances and bearings to previously established transponders onshore. Although these systems are capable of excellent absolute accuracy, they have many disadvantages, including high cost, daily initialization and/or calibration of the system, the necessity for each transponder to be placed over an accurately surveyed point onshore, and the requirement that transponders be moved to remain in line of sight with the sampling vessel.

Global Positioning System (NAVSTAR GPS)

GPS represents a rapidly evolving technology that calculates positions by triangulating on three or more very high-orbit satellites. GPS currently provides nearly continuous 2- and 3-dimensional coverage.

Differential GPS (DGPS) is a variation of standard GPS in which a reference receiver is used to greatly enhance the accuracy of standard GPS. The reference receiver is placed at a precisely known location where GPS data are simultaneously collected and compared with that of a remote receiver, such as on the survey vessel. The reference unit calculates correction factors that are then transmitted to the remote receiver(s). DGPS can be operated in either a real-time mode or in a post-survey mode. In the real-time mode, the differentially corrected position information is available to the operator of the system instantaneously. This feature is a necessity if it is important for sampling to occur at an accurately known, predetermined location. In the post-survey mode, position information is logged by the equipment, but the correction algorithm is not applied to the data until after the survey. The latter mode may be adequate if it is not important to know the precise location at the time of sampling, but only to be able to accurately locate the sampling stations after the fact.

To control the quality of position data obtainable by users, the U.S. Department of Defense, for national security reasons, has the ability to activate a feature referred to as "selective availability." This feature allows the intentional degradation of GPS signals produced by transmitting slightly erroneous data. Selective availability was activated on a continuing basis on March 25, 1990. The standard GPS signal with selective availability provides accuracies of ± 100 m. DGPS corrects for the effects of selective availability and is capable of absolute accuracies of < 1 m.

GPS systems also have the ability to obtain accurate altitude and time information. The time feature is useful for linking geographic positions to other computer-logged data, such as seismic or bathymetric survey data.

There are many advantages of the DGPS, including very good, absolute accuracy (< 1 m); no required shore access (except for establishing a reference station that can be anywhere from 20 to 100 miles [160 km] away); minimal operator involvement; ability to coordinate positions with simultaneously collected data using time as the integrating element; capability for real-time position determination; and the ability to log data for later processing to improve the accuracy.

The disadvantages of DGPS may include the need to buy an additional receiver to act as a reference station, and the requirement that receivers retain line of site with the satellites being used for position determinations, although this is seldom a problem.

Field Positioning System Used in the ARCS Program

After investigating the various positioning technologies available, DGPS was determined to be the most appropriate for establishing sampling locations in the ARCS Program. Both real-time and post-survey DGPS were used for position determinations during ARCS Program sediment sampling surveys. Because the primary role of the positioning system was to determine where samples had been collected, post-survey DGPS was the predominant method used. Real-time DGPS was used only when it was necessary to position the survey vessel at an accurately known, predetermined position. The procedures for collecting data were similar for both real-time and post-survey DGPS, with the exception of the required maintenance of the radio data link for real-time DGPS.

Post-survey data processing involved analyzing the logged GPS data with differential correction software, which, along with data filtering and smoothing, used the reference station data to calculate corrected position data for the mobile station. After processing, the corrected position data were available in a standard latitude/longitude format.

DGPS proved to be a very accurate and efficient means of collecting positional data for the ARCS Program. Although the incomplete satellite constellation caused some scheduling problems early on, the launching of additional satellites soon solved this problem. The current satellite constellation supports 24-hour, 2- and 3-dimensional positioning.

The ability to acquire position fixes in areas of massive shore structures was an unexpected benefit. This ability can be attributed to the number of satellites available and their varied and changing positions. There are some areas where satellite signal acquisition is not possible, such as under bridges; positions for these obstructed points can be determined by calculating a relative position from a nearby absolute position and using geometry to calculate the offset of the relative point from the absolute point. When collecting continuous data, GPS navigational software uses sophisticated data processing techniques involving a Kalman filter to handle signal dropout.

As DGPS receiver prices, size, and power requirements continue to decrease and features such as reference station services and geographic information system (GIS)-compatible data formats become more available, the advantages of DGPS will continue to increase. DGPS is therefore recommended for field surveys in other Great Lakes AOCs.

SEDIMENT SAMPLING PROCEDURES

The field practices and methods by which sediment samples are collected form the foundation for the quality of the sediment study being conducted. Prior to commencing field operations, thought must be given to the DQOs of the project (see Chapter 2). Pertinent considerations include the type(s) of sediment samples that will be required and how they will be analyzed.

In all field operations, the primary goal of sediment sampling is to collect a sample that accurately represents the sediment condition *in situ*. Specific sediment collection and preservation requirements will depend on the study. For example, benthic community analyses require different sediment collection and preservation methods than those for chemical analyses.

The type of sediment collection technique chosen will depend on several considerations, including the study objectives, the numbers and types of analyses required, the available sampling vessel, weather conditions, the type(s) of sediment being collected, and the depth to which sediment is to be sampled.

There are two general types of sediment samplers, grab samplers and sediment corers. Grab samplers are routinely used to collect surficial sediment samples, as are usually required for physical and chemical analyses and benthic invertebrate characterization. Sediment corers can provide less disturbed samples and profiles of subsurface sediments, in which *in situ* conditions are preserved, although the surface layer may be disturbed from compaction or being eroded immediately prior to impact by the water pushed ahead of the coring unit. Distortion of the sediment core can also occur, caused by compaction or stretching of the sediment during collection. Sediment corers are most often used for assessment of environmental contaminants in subsurface sediments, for evaluation of sediment for dredging and disposal, and in geochemical surveys.

The advantages and disadvantages of various recommended sediment samplers are summarized in Table 3-2. In-depth discussions of sediment samplers can be found in Baudo et al. (1990), Burton (1992b), Mudroch and MacKnight (1991), APHA (1989), and ASTM (1990).

Grab Samplers

Grab samplers are usually designed as a box with a set of jaws, or a rotating bucket, that takes a wedge-shaped bite out of the surface sediment. These samplers allow the collection of small or large sample volumes and can be effective over a wide range of surficial sediment types. They are easy to use, and the smaller grab samplers allow hand deployment and retrieval from a small sampling platform. Disadvantages of the grab sampler include the uncertainty of the depth of sediment penetration and the loss of sample integrity when the sampler is open. Grab samplers also do not disturb the surface sediment significantly unless they overpenetrate. Penetration depth of grab samplers can be highly variable, depending on sampler design and sediment composition.

When selecting a grab sampler, the method of retrieval, the type of sediment, the required sample volume, and the strength of currents at the site should be considered.

TABLE 3-2. ADVANTAGES AND DISADVANTAGES OF VARIOUS SEDIMENT SAMPLERS

Sampler	Advantages	Disadvantages
Hand and gravity corers	Maintain sediment layering of the inner core. Fine surficial sediments retained by hand corer. Replicate samples efficiently obtained. Removable liners. Inert liners may be used. Quantitative sampling allowed.	Small sample volume. Gravity corer may result in loss of fine surficial sediments. Liner removal required for repetitive sampling. Not suitable in coarse-grain or consolidated sediments.
Box corer	Maintains sediment layering of large volume of sediment. Surficial fine sediments retained relatively well. Quantitative sampling allowed. Excellent control of depth of penetration.	Size and weight require power winch; difficult to handle and transport. Not suitable in consolidated sediment.
Vibrocorer	Samples deep sediment for historical analyses. Samples consolidated sediments.	Expensive and requires winch. Outer core integrity slightly disrupted.
Ekman or box dredge	Relatively large volume of sediment may be obtained. May be subsampled through lid. Lid design reduces loss of surficial sediments as compared to many dredges. Usable in moderately compacted sediments of varying grain sizes.	Loss of fine sediments may occur during sampling. Incomplete jaw closure occurs in coarse-grain sediments or with large debris. Sediment integrity disrupted. Not an inert surface.
Ponar grab	Commonly used. Large volume of sediment obtained. Adequate on most substrates. Weight allows use in deep waters. Good sediment penetration.	Loss of fine sediments and sediment integrity occurs. Incomplete jaw closure occurs occasionally. Not an inert surface. Heavy and requires a winch.
van Veen or Young grab	Useful in deep water and on most substrates. Young grab coated with inert polymer. Large sediment volume obtained.	Loss of fine sediments and sediment integrity occurs. Incomplete jaw closure possible. van Veen grab has metal surface. Young grab is expensive. Both may require a winch.
Petersen grab	Large sediment volume obtained from most substrates in deep waters.	Loss of fine sediments and sediment integrity. Not an inert surface. Incomplete jaw closure may occur. May require winch.
Orange-peel grab	Large sediment volume obtained from most substrates. Efficient closure.	Loss of fine sediments and sediment integrity. Not an inert surface. Requires winch.
Shipek grab	Adequate on most substrates.	Small volume. Loss of fine sediments and sediment integrity. Not an inert surface.

Source: Adapted from Burton (1992).

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Sediment Corers

Sediment coring is generally accomplished by inserting a rectangular or cylindrical tube into the sediment and withdrawing a sediment core. Sediment corers range in size and complexity. Small push corers and small gravity corers can be retrieved by hand and used from a small boat. Larger and more complicated corers such as piston and vibro-corers require a lifting boom, a winch, larger sampling vessels, and more field crew.

Problems in sediment coring are often associated with inadequate sediment penetration, core distortion, or inadequate core retention during corer retrieval. Heavy weights or vibrations applied to the core tube can improve penetration in dense sediments. Various types of core "catchers" installed at the lower end of the core tube can prevent sample loss in uncompacted sediments; however, these catchers can also impede penetration in compacted sediment. Corer deployment can also be difficult under certain conditions. The vessel should be 3-way anchored to maintain a steady position while the corer penetrates into the sediment. Trying to core in a strong current or wind, even with the vessel properly anchored, can result in the corer entering the sediment at an angle or core tubes being bent during retrieval.

Sediment Samplers and Procedures Used in the ARCS Program

During the ARCS Program, Ponar and van Veen grab samplers were used to collect surface sediments. When sampling for benthic invertebrates, it was important to collect these benthic samples before collecting other samples to minimize disturbance to the benthic community prior to collection of the sample. The 0.05-m^2 Ponar grab sampler (23 cm $\times$ 23 cm, 529 cm^2, 23 kg; Wildlife Supply Company, Saginaw, Michigan) was designed to penetrate the sediment by weight alone and to sample about the same amount of sediment with each cast. In the ARCS Program, a sediment penetration depth of 10–20 cm was desired. The Ponar grab sampler was designed for use in lakes, reservoirs, rivers, and estuaries with soft or hard sediments. It is equipped with No. 30 mesh brass screens on the open ends of its jaws to minimize loss of material. The van Veen grab sampler (Kahl Scientific Instrument Corporation, El Cajon, California) samples a surface area of 1 ft^2 (0.1 m^2) and has a capacity of 5 gal (20 L). The Ponar grab sampler was easier to handle than the van Veen grab sampler, but collected smaller samples. The van Veen grab sampler proved to be much more efficient for collecting large volumes of sediment, although it requires a power winch to operate safely. The van Veen grab sampler penetrates to a greater depth than the Ponar grab sampler.

Where collection of large volumes of sediment is not as important, it may be possible to use the petite Ponar grab sampler. The petite Ponar grab sampler is essentially the same as the full-sized Ponar grab sampler, but it is smaller (15 cm $\times$ 15 cm, 225 cm^2, 6.8 kg). The advantages and limitations of the petite Ponar grab sampler are the same as those for the full-sized Ponar grab sampler, with the exceptions that the petite sampler is considerably lighter than the full-sized sampler, does not penetrate clay substrates as well, and is not as efficient in flowing water with a velocity of ≥ 1 m/sec (Klemm et al.

1990). The petite Ponar grab sampler is designed to penetrate the sediment to depths of 5-15 cm. The main advantage of using this sampler is that it can be operated without a boat or winch.

For the collection of sediment grab samples during the ARCS Program, the vessel was first anchored and its position determined. As multiple grab sampler casts were made, the vessel was slightly repositioned as necessary to ensure that only surficial sediments were collected.

Collection of sediment core samples during the ARCS Program was preceded by dropping a grab sampler or probing the bottom near the area where sample collection was desired, to determine whether soft sediments were present. The vessel was then securely anchored by triple anchoring. Next, the water depth was measured to determine the approximate depth at which the corer encountered the sediments. For vibrocoring, the core unit was allowed to penetrate until the tube no longer penetrated the sediments (i.e., until refusal) or until the vibrocore head was near the sediment surface.

Two vibrocoring devices were used in the ARCS Program. The first, assembled by the staff of the Large Lakes Research Station (LLRS), used a Wacker® Model M3000, 3-horsepower, electro-mechanical vibrator (Wacker Corporation, Milwaukee, Wisconsin). Its flexible shaft was attached to a custom-made, stainless-steel core head with a Model H45 vibrator head. The core head accepted 3-in. (7.6-cm)-diameter core tubes. This unit, although fairly light (the vibrator head weighed 18 lb [8.1 kg]) and portable, was not sufficiently powerful to collect cores more than 5-6 ft (1.8-2 m) long.

The second vibrocoring unit was a Rossfelder® Model P-4 Vibrocorer (Rossfelder Corporation, La Jolla, California). The vibrating head consists of two, 2-horsepower electric (3-phase) motors in a water-tight housing, and it produces a centrifugal force of 7,000 lbs (15.7 kiloNewtons) and a mono-directional frequency of 3,400 vibrations per minute. An aluminum core tube (4 in. [10 cm] in diameter; up to 20 ft [6 m] long) is inserted into the vibrating head, and the entire assembly is lowered into the water. The Model P-4 unit is heavy (i.e., 250 lbs; 113 kg); therefore, a vessel like the R/V *Mudpuppy* must be used to maintain vessel balance and provide adequate lift to break the corer out of the mud and retrieve it. Vessels like the R/V *Mudpuppy* require experienced crew for safe, efficient operation of the boat and equipment.

The Model P-4 Vibrocorer proved powerful enough to collect cores more than 16 ft (5 m) in length, even when they included several feet of clay. However, no cores much longer than 16 ft were collected, even when the 20-ft core tube fully penetrated the bottom. One obvious reason for not collecting samples throughout the entire depth of penetration of the core tube was that the cross-sectional area inside the core nose was about 10 percent less than the cross-sectional area of the core tube itself, thereby reducing the collected sediment volume by that much. Another reason may be that friction inside the core tube can exceed the bearing strength of soft sediments, resulting in a plugged core tube that continues to penetrate without collecting more sediment.

Finally, sediments can compress when cored, but this is less of a problem with large-diameter vibrocorers than with gravity or piston corers.

Hard surface and subsurface debris (e.g., rock, pavement) can prevent collection of a core or even damage or destroy the core tube. These materials are not uncommon in the industrialized rivers and harbors of the Great Lakes.

Conclusions

For the collection of surface sediment samples, either the Ponar or van Veen grab sampler is recommended. The van Veen grab sampler may be more appropriate when large volumes of sediment are needed for analysis.

Vibrocoring is a versatile and efficient method for collecting long sediment cores throughout Great Lakes AOCs or similar harbors. Although rotary drilling methods could yield longer cores even in hard-bottom areas, they were not considered to be a feasible alternative to vibrocoring for several reasons. One reason is the greater cost of the drilling rig and barge support. Another is that vibrocoring is more mobile and practical for close-quarters sampling in shallow areas. A vessel similar to the R/V *Mudpuppy* is a relatively small craft that provides better access to congested harbor sites.

Although the Model P-4 Vibrocorer worked extremely well and appears to be the only unit capable of consistently collecting long cores, it was not without limitations, which included:

- Its 3-phase, 230-volt power, which required the use of a special generator

- Its weight (the vibrating head weighs 250 lb [113 kg], and with a 15-ft [5 m] core tube full of sediments the entire assembly weighs over 400 lb [180 kg]).

A rigid tube core liner (e.g., cellulose acetate butyrate [CAB]) should be used to easily retrieve and store core sections. Prior to commencing sampling operations, a plan for subsampling the cores should be developed indicating the desired sampling intervals; however, flexibility must be maintained to allow for plan modifications in the field as dictated by observed core strata.

Future refinements to sediment coring include the application of suction to the upper end of the core tube during coring, which may result in the retrieval of longer cores, and the development of in-field, real-time analyses (i.e., screening-level analyses, see Chapter 4) that will provide data to guide subsequent sampling.

Aside from vibrocorers, few coring devices were considered suitable for use in the ARCS Program. Box cores are generally heavy (>500 lb [230 kg]) and their cores are usually ≤1.5 ft (0.5 m) long. Gravity or hand-held corers will seldom penetrate greater than

3 ft (1 m). Piston corers are awkward to deploy in shallow waters, such as those found in Great Lakes AOCs, and are less able to penetrate clay or gravel layers.

Proper identification of individual cores and associated subsamples is especially important for sediment projects because of the potential for collection of large numbers of samples, especially when various laboratories will be analyzing splits of those samples. Each sample should be assigned a unique sample number. Figure 3-2 shows an example sample numbering system used during the ARCS Program. Individual laboratories often assign in-house numbers to their samples as necessary, but all interlaboratory data transfers should use the original sample number.
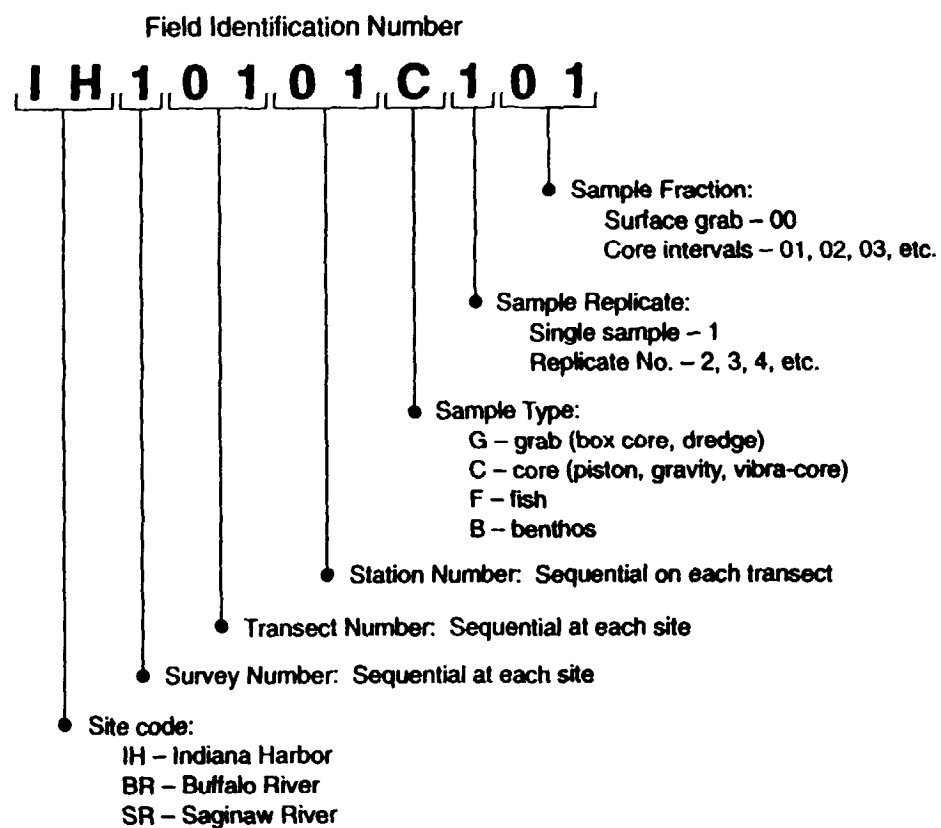
The visual characteristics of each sediment core, total length, position of layers within the core, and the color, texture, and composition of the material should be recorded in a core observation log immediately upon collection. Much of this information is qualitative or subjective and could vary from one observer to another; for consistency, only one or two workers should describe the cores during any one survey.

Describing the cores is relatively simple; however, several cautions and techniques that were learned during the ARCS Program can be used to improve the quality of this information. Although polarized sunglasses are often worn when working on the water, they can influence color vision; therefore, all core descriptions should be conducted without them. To determine the color of sediments, a standard color scale can be used. A typical set of Munsell color charts was tried, but none depicted the colors found in these aquatic sediments. However, other Munsell pages are available and could be used to describe the colors of Great Lakes sediments. Monitoring sediment odor, although useful for detecting petroleum hydrocarbons, poses an unacceptable risk of inhalation exposure, and should not be performed. Descriptions of sediment texture and composition were improved when the "ribbon test" (a texture-by-feel test) was applied to distinguish between clay and compressed silt (Brady 1974). To conduct the ribbon test, a small piece of suspected clay is rolled between the fingers while wearing protective gloves. If it easily rolls into a ribbon (or rod) over 1 in. (2.5 cm) long, it is clay; if it breaks apart, it is silt.

During the ARCS Program, the core description process was initially videotaped, with the intent to later inspect the videotape if questions or data anomalies arose. Later, color photographs were used to record the core appearance in overlapping frames at approximately 30-cm intervals. This provided a visual record of core zonation.

FIELD PROCESSING OF SEDIMENT SAMPLES FOR PHYSICAL AND CHEMICAL ANALYSES

Sample processing (i.e., sectioning, subsampling, and packaging samples for shipment to the laboratory) can be conducted onboard the vessel or from a shore-based sampling area. The advantages of onboard processing are 1) it takes less crew to perform a sampling survey and 2) the excess sediment can be dumped back into the water after the

Field Identification Number

I H 1 0 1 0 1 C 1 0 1

- Sample Fraction:
  Surface grab – 00
  Core intervals – 01, 02, 03, etc.

- Sample Replicate:
  Single sample – 1
  Replicate No. – 2, 3, 4, etc.

- Sample Type:
  G – grab (box core, dredge)
  C – core (piston, gravity, vibra-core)
  F – fish
  B – benthos

- Station Number: Sequential on each transect

- Transect Number: Sequential at each site

- Survey Number: Sequential at each site

- Site code:
  IH – Indiana Harbor
  BR – Buffalo River
  SR – Saginaw River

Note: Supplemental information is recorded on the field data sheets.

Figure 3-2. Example sample numbering system used in the ARCS Program.

subsampling is complete. Dumping the sediment back into the water body lessens the costs for transportation, storage, and disposal of samples. The main advantage of shore-based processing is that it allows more samples to be collected during a sampling day, because time is not taken for sample processing by the sampling crew. However, shore-based processing requires disposal of excess sediments (i.e., returning the excess sediments to the water may not be an option). During the ARCS Program, buckets were used to transport bulk sediments to shore, and plastic bag liners were used to minimize the need for cleaning the buckets between samples. Cores were transported in capped sections of the CAB liner.

Sample processing requirements for a project are specific to the goals of the study and should be described in a sampling plan. Factors to be addressed include the sample size to be collected, the number and type of subsamples to be collected from each sample, the types of analyses to be conducted, the analytical resources available, and sample storage requirements and preservation techniques. Required container types, preservation techniques, and holding times for sediment samples should follow recommendations in 40 CFR 136.3, Table II. A summary of the container types, preservation techniques, and holding times appropriate for commonly measured sediment parameters is provided in Table 3-3. However, 40 CFR § 136.3 does not allow for freezing or freeze-drying. In addition, the sampling plan should include specific information as to which samples will be associated with various quality assurance samples (e.g., if a matrix spike will be performed on a sample, double the normal sample volume may be required).

When subsampling cores, two methods are commonly used. The first method is to subsample discrete layers. For example, during the ARCS Program, the cores were either cut into 2-ft sections or subsampled by visual strata. Each section was homogenized and subsampled from the homogenate. The second subsampling method is to split the core longitudinally (either as a whole or cut into subsections). Subsamples are then selected by homogenizing or collecting entire visually homogeneous layers. Subsampling the homogenate from 1- to 3-ft intervals is generally recommended, because most remediation scenarios will involve dredging, and dredging accuracy is approximately 1-3 ft. However, it may make sense to define important boundaries accurately if dredging is warranted. The second method of subsampling cores should be employed if the intent is to characterize visually distinct layers throughout the core. In some areas, however, this can lead to a tremendous number of samples per core.

During collection of sediment samples, homogenization is generally necessary to obtain a representative sample and to provide a sufficient volume of sediment for required testing. Homogenization is performed by mixing sediments in a clean, stainless-steel bowl with a stainless-steel spoon until visually homogeneous. The mixing time varies, increasing inversely with sediment water content. Care must be taken to minimize contamination, both in the field and laboratory, and to reduce exposure to oxygen if acid-volatile sulfide (AVS) is a parameter of interest. Due to sample volume requirements of the ARCS Program, however, large sediment composite samples were homogenized in the field without protecting the sediment from oxidation. Nonetheless, there was generally far more AVS on a molar basis than the divalent metals (cadmium, copper,

TABLE 3-3. RECOMMENDED SAMPLE SIZES, CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Media/Analyte	Sample Size (g)[a]	Container[b]	Preservation Technique	Maximum Holding Time[c]	Maximum Extract Holding Time
Sediments					
Particle size	100–150[d]	P,G	Cool, 4°C	6 months	--
Total solids	50	P,G	Freeze	1 year	--
Total volatile solids	50	P,G	Freeze	1 year	--
Total organic carbon	50	P,G	Freeze	1 year	--
Oil and grease	100	G	Cool, 4°C, HCl; freeze	28 days 6 months	--
Acid-volatile sulfides	15	P,G	Cool, 4°C	14 days	--
Total sulfides	50	P,G	Cool, 4°C, 1N zinc acetate	7 days	--
Semivolatile organic compounds	50–100	G	Freeze	1 year	40 days
Pesticides and PCBs	50–100	G	Freeze	1 year	40 days
Mercury	1[e]	P,G	Freeze Freeze-dried[f]	28 days 2 years[f]	--
Methylmercury	20	P,G	Freeze	28 days	--
Butyltin compounds	50–100	G	Freeze	1 year	40 days
Metals (except mercury)	50[e]	P,G	Freeze	2 years	--
Tissues (whole)					
Semivolatile organic compounds	--[g]	A	Freeze	1 year	40 days
Pesticides and PCBs	--[g]	A	Freeze	1 year	40 days
Mercury	--[g]	A	Freeze	28 days	--
Methylmercury	--[g]	A	Freeze	28 days	--
Metals (except mercury)	--[g]	A	Freeze	2 years	--

TABLE 3-3. (cont.)

Media/Analyte	Sample Size (g)[a]	Container[b]	Preservation Technique	Maximum Holding Time[c]	Maximum Extract Holding Time
Tissues (after resection)					
Semivolatile organic compounds	25	G,T	Freeze	1 year	40 days
Pesticides and PCBs	25	G,T	Freeze	1 year	40 days
Mercury	0.2[e]	P,G	Freeze; freeze-dried[f]	28 days 2 years[f]	--
Methylmercury	20	P,G	Freeze	28 days	--
Metals (except mercury)	6[e]	P,G	Freeze	2 years	--

[a] Recommended field sample sizes for one laboratory analysis. If additional laboratory analyses are required (e.g., replicates), the field sample size should be adjusted accordingly (i.e., multiply the sample size by 4 to account for laboratory quality control samples). For tissue samples (after resection), studies using specific organs may require more tissue.

[b] A - wrapped in aluminum foil
G - glass with Teflon®; pre-cleaned jars can be purchased
P - polyethylene
T - PTFE (Teflon®).

[c] Suggested holding times; no USEPA criteria exist for these variables in these media. The holding time of 1 year for semivolatile organic compounds exceeds the USEPA criterion of 14 days; every effort should be made to analyze the sample as soon as possible.

[d] Sandier sediments require larger sample sizes than do muddier sediments.

[e] Wet weight.

[f] Standard reference materials prepared by the U.S. National Institute for Standards and Technology (U.S. NIST) are freeze-dried and can be stored for at least 2 years. It should, therefore, be acceptable to freeze-dry these samples and hold them for a similar period (Crecelius 1994, pers. comm.)

[g] Whole tissues are not generally recommended for analysis.

lead, mercury, nickel, silver, and zinc) that precipitate as sulfides (Ingersoll et al. 1993). AVS is an important parameter for determining the bioavailability of divalent metals (see additional discussion in Chapter 5). AVS is also subject to destruction if samples are improperly handled; therefore, efforts should be made to maintain the *in situ* AVS concentrations. Ideally, the sediment sampling and homogenization process could be conducted in the field in a nitrogen-filled glove box or glove bag to reduce sulfide oxidation. However, this method may be unpractical. An alternative recommended method for sampling sediments for AVS is to transfer an unhomogenized aliquot of the sediment from the sampling device to a glass jar with minimum disturbance and contact with air. The jar should be filled to the brim to exclude air and then capped and stored at 4°C (freezing may break the jar). The AVS analysis should be completed within 2 weeks. Similar procedures should be followed for collecting unhomogenized aliquots of sediment for analyses of total sulfides and volatile organic compounds.

Sample jars should be double wrapped in plastic bags prior to shipment and packed in such a manner as to prevent jar breakage. Ice chests should be used to store and ship the samples. By changing freezer packs once a day, it is generally possible to keep the samples cooler than ambient temperatures until shipment by overnight express. Samples should be kept at 4°C until arrival at the laboratory. Methods employed might include ice, freezer packs, or dry ice. Freezer packs have the advantage of not creating a water problem with melting as ice does. When using dry ice, the samples should be insulated from the dry ice using paper or plastic bubble wrap to prevent sample freezing. It is also necessary to be cognizant of possible transport restrictions regarding the use of dry ice, especially when transporting by air.

When transporting samples, all U.S. Department of Transportation packaging regulations should be followed. If field crews are transporting the samples to the laboratory, the driver should be provided with a manifest listing all samples and the preservation methods. If any hazardous chemicals are used to preserve the samples, the driver should also be provided with Material Safety Data Sheets.

Chain-of-custody forms should accompany the samples at all times. As sediment samples are received from the field, they should be immediately logged into a sample tracking system and the chain-of-custody forms checked against the actual contents of the coolers. The samples should then be placed in a continuously monitored cold storage room until subsampled for analysis. See Chapter 2 for additional details on QA/QC for chemical analyses.

FIELD PROCESSING OF SEDIMENT SAMPLES FOR BENTHIC COMMUNITY ANALYSES

During the ARCS Program, benthos samples were collected using a Ponar or van Veen grab sampler, sieved aboard the R/V *Mudpuppy*, and then shipped to the laboratory for taxonomic analysis. (See Chapter 7 for detailed discussion and recommendations on sampling methods and study objectives.) Each sample was sieved through a 500-μm

brass screen, using station water to wash the material. This operation was greatly facilitated by the wash table on the deck of the R/V *Mudpuppy*. Material retained by the sieve was transferred to a 500-mL glass jar and preserved with 10-percent buffered formalin. Sample jars were double-wrapped in plastic bags before shipment; nevertheless, a few jars broke during shipping.

Ancillary information collected in the field included percent fullness of the Ponar sampler and water chemistry information (dissolved oxygen, conductivity, temperature, and oxidation/reduction potential) measured with a Hydrolab® sonde positioned 1 m above the bottom.

FIELD PROCESSING OF SEDIMENT SAMPLES FOR TOXICITY TESTING

In general, the sediments collected for toxicity testing will be subsamples of homogenized sediment samples that are also chemically analyzed. During the ARCS Program, the sediments intended for toxicity testing were processed by the same methods described above for sediment samples subjected to physical and chemical analyses. The volume of sediment collected for toxicity testing was a function of the number and type of tests to be conducted. The sediment was placed in high-density polyethylene jars, labeled, and transferred in ice chests to the toxicity testing laboratory by overnight express. Sediments intended for toxicity testing should not be frozen.

SEDIMENT CHARACTERIZATION BY REMOTE SENSING

To maximize the effectiveness of the sampling design, it is recommended that a preliminary survey be conducted to determine where fine-grained sediment deposits are located. Contaminants tend to be associated more with fine-grained sediments (e.g., silts and clays) than with coarser-grained materials (e.g., sands and gravels). Fine-grained sediments can often be found by probing the bottom at specific locations in shallow areas, or by taking small grab samples. In a more systematic way, remote sensing technology may be used for cost-effective characterization and mapping of sediment types over broad areas in harbors and rivers, as it is currently used in offshore waters. However, these techniques need more development for work in the shallow waters typical of Great Lakes rivers and some harbors.

The objectives of remote sensing sediment characterization in the ARCS Program were:

- To map the spatial extent and thickness of post-glacial bottom sediments

- To qualitatively characterize mapped sediments in terms of their clay content

- To qualitatively characterize the sediments in terms of their degree of compaction or hardness

■ To provide a database of qualitative sediment characteristics to assist in the selection of sediment coring sites.

The goals associated with these objectives were:

■ To ensure that the locations of principal sediment types would be directly sampled for chemical analysis

■ To determine whether sediment contamination is associated primarily or entirely with selected sediment deposits that have been geophysically mapped, or whether the sediment contamination is distributed independently of the mapped sediment deposits.

Acoustic subbottom profiling and electrical resistivity are two geophysical profiling techniques that can be used for remote sensing sediment characterization, although these techniques require further development before they can be routinely implemented in investigations of Great Lakes AOCs.

Acoustic Subbottom Profiling

Acoustic subbottom profiling of sediments makes use of reflected sound waves from different subsurface sediment layers (Figure 3-3). These layers, which exhibit interfaces of different elasticity and density, can sometimes be distinguished as distinct layers within the profile trace. Uncompacted, fine-grained sediments demonstrate high porosity and are poor acoustical reflectors. Coarse-grained sediments exhibit lower porosity and tend to be good reflectors (Guigné et al. 1991).

Interpretation of the seismic profile is accomplished by "ground truthing" using sediment cores collected at selected points along the ship's track followed during the seismic survey. The visual description of core stratigraphy is compared to the seismic profile for that position. A comparison of the core profile to the seismic profile allows interpretation of seismic reflectors (layers) as sediment types, such as gravel, sand, silt, and clay. The characterization of sediment stratigraphy between cores is mapped using the interpreted seismic profiles, providing a complete picture of sediment distribution in the study area.

Acoustic subbottom profiling has limitations. In shallow water, multiple echoes from the water and bottom surface may obscure echoes from deeper sediments. The gas content of sediment also reduces the effectiveness of acoustic subbottom profiling by prohibiting acoustic signal penetration, absorbing or scattering most of the acoustic energy back to the surface. During the ARCS Program, acoustic subbottom profiling was unsuccessful, probably due to multiple reflectors (see Figure 3-3) and attenuation and scattering of the sound waves by gases contained in the sediments.

Source   Receiver

Water surface

Sea bed

Reflector 1
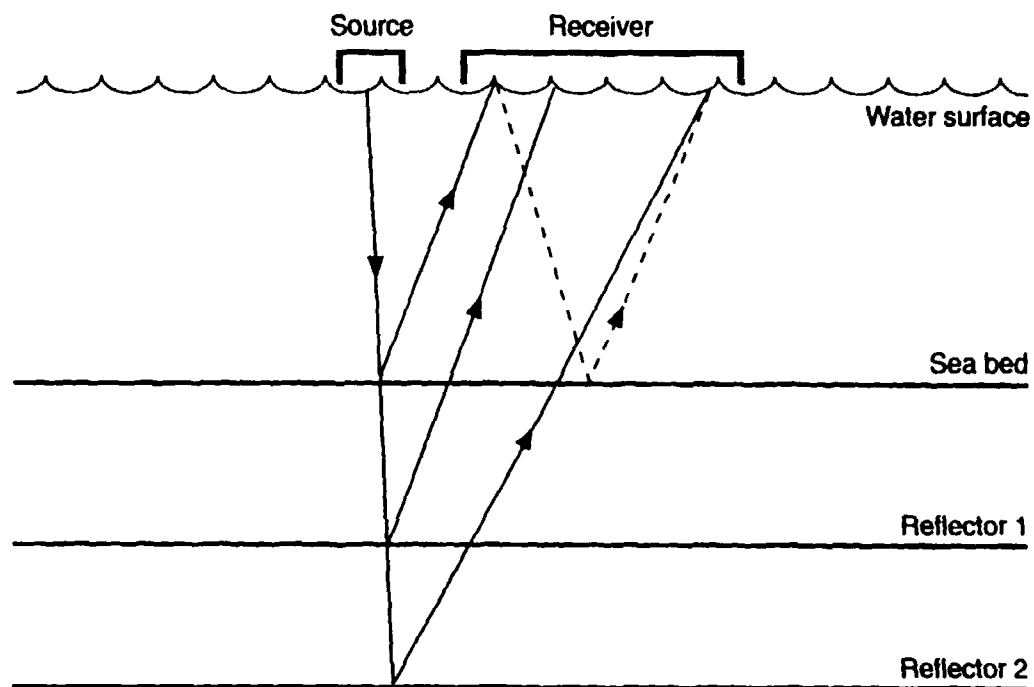
Reflector 2

LEGEND

– – – – Multiple

———— First return

Sound produced at the source reflects off the sea bed surface, reflector 1, and reflector 2, which are areas of rapid density change. The receiver captures the reflected sound waves. A multiple sound wave is received at the same time as the reflector 2 sound wave, obscuring reflector 2 on the seismic record.

Figure 3-3. Diagram of acoustic subbottom profiling.

Electrical Resistivity (Conductivity) Profiling

Electrical resistivity (conductivity) profiling is a common geophysical technique used in pollution-related studies on land. The electrical resistivity of sediments is primarily a function of their porosity and pore fluid chemistry. For clay-rich sediments, the clay mineralogy is also a significant factor. It is generally not possible to separate the effects of porosity, pore fluid chemistry, or mineralogy on resistivity measurements.

The objectives of electrical resistivity or conductivity surveys are the same: a lateral and vertical mapping of sediments with similar electrical properties. Comparison of the electrical properties of the sediments with actual cores provides a basis for associating the electrical properties with specific sediment types to assess sediment deposit hardness. Resistivities of approximately 10 to 40 ohm-meters are generally associated with wet clays, while resistivities in the range of 100 to 200 ohm-meters are generally associated with wet clean sand (Telford et al. 1976).

While not as useful by themselves, electrical resistivity surveys could be used to supplement acoustical subbottom profiling.

Conclusions

Acoustically turbid sediments (i.e., sediment with acoustically unresolvable layering) were found at all three ARCS priority AOCs where acoustic subbottom profiling was applied, preventing demonstration of this technique for remote sensing sediment characterization. Other forms of remote sensing such as ground penetrating radar or induced conductivity still need to be explored. A suite of remote sensing techniques, including acoustic subbottom profiling and electrical resistivity, may be needed to perform reliable mapping of sediment deposits in harbors and rivers, although more research needs to be conducted.

Surface hardness classification using acoustical first return amplitudes was shown to be a promising remote sensing technique, but needs further development. This method should be refined with algorithms developed to allow classification of rock, sand, silt, and clay sediment types, although this will only classify surface sediments. Research in acoustical sediment classification continues (Schock et al. 1986; Guigné et al. 1991; Sjostrom et al. 1992) and may yet prove useful in other Great Lakes AOCS.

PROCEDURES FOR CHARACTERIZATION OF CONTAMINATED SEDIMENTS

3.1 Introduction

Characterization of contaminated sediments begins with the identification of contaminants present. While a list of contaminants is important, a description of the vertical and horizontal distributions of the contaminants within the sediments is also necessary due to the heterogeneity of most sediments. Characterization of the sediments is also important, as sediment characteristics will have profound effects on contaminant availability (see Chapter One) and should impact remediation decisions. Sediment characterization should include physical and chemical characteristics but also distributions of these within the site of concern. Modeling sediment transport and contaminant fate and transport will give additional insight into sediment characteristics. Key to efficient and economical characterization is the development of a sampling plan and the selection of the proper sampling method.

3.2 Sampling Plan

In order to properly sample and characterize contaminated sediments, extensive planning must first be done. The sequence in the planning stage should include:

1. Identification of sampling purposes and objectives.
2. Compilation of available data on the site of concern.
3. Collection of preliminary field data.
4. Development of a detailed sampling plan.

Developing a sampling plan appropriate for the site and sampling objectives increases the quality of the site characterization and minimizes characterization costs. Unfortunately, due to site variability, a systemized sampling plan applicable to all sites is not feasible.

3.2.1 Identification of Sampling Purposes and Objectives

The scope of effort is dependent on this decision. Purposes for sediment sampling and testing might include:

1. Determine distribution of specific contaminants.
2. Determine sediment contaminant mobility.
3. Determine existing impacts on aquatic/benthic fauna.
4. Determine disposal alternatives (regulatory).
5. Determine disposal alternatives (treatability).

No single sampling/analysis plan will serve all these purposes equally well.

3.2.2 Compilation of Available Data

This data should include the following:

1. Water depths/tidal fluctuations.
2. Obstructions (bridges, pipelines, etc.).
3. Access sites for mobilizing equipment.
4. Sediment depths (dredging or construction history).
5. Sources of contaminants (point and non-point) and other factors affecting contaminant distributions.
6. Hydraulic/other factors affecting sediment distribution.
7. Historic sediment quality data.
8. Survey benchmarks (for referencing sediment and water elevations).

3.2.3 Collection of Preliminary Field Data

Given the costs of sampling and of laboratory analyses, it is prudent to conduct some cursory field studies before developing the sampling and analysis plan. Such studies should be mandatory where any existing physical information is lacking. The amount of time and money that can be saved by simply visiting the site in a small boat and poking a long stick in the mud cannot be overestimated.

3.2.4 Development of a Detailed Sampling Plan

Once the first three steps have been completed, the specifics of the sampling and analysis plan can be developed. These include contractual, logistical, and statistical considerations. The plan developed as a part of step four should include details on:

1. Locations of samples (lateral and vertical).
2. Types of samples (grab or core).
3. Number and volumes of samples required.
4. Sampling procedures and equipment.
5. Supporting vessels/equipment.
6. Types of analytical tests required.
7. Quality Assurance Program Plan (QAPP) for sampling and analysis.
8. Cost estimate.

3.3 Sampling Methods

There are a number of sampling devices that are presently being used to collect samples. Choosing the most appropriate sediment sampler for the study will depend on the requirements of the sampling plan. Attention should be paid to sample linings: metal linings may introduce metal contaminants into the sediment samples; plastic linings may introduce organic contaminants into the sediment samples.

Biological collections are generally accomplished by trawling or dredging. Sediment collections have been made with spoons, scoops, trowels, core samplers, and grab samplers.

3.3.1 Spoons, Scoops, and Trowels

Spoons, scoops, and trowels are only useful in shallow water. They are less costly than other samplers, easy to use, and may be useful if numerous samples are intended; their low cost allows disposal between sample sites. In general, however, these devices are somewhat undesirable because the reproducibility of sampling area, depth, and volume from one sampling site to another is poor. They also tend to disrupt the sediment during sampling.[1]

3.3.2 Core Samplers

These may be used in both shallow and deep aquatic systems on a variety of substrate conditions. Core samplers are generally preferred over other samplers because (1) core samplers can sample to greater depth, (2) core samplers maintain the complex integrity of the

sediment, and (3) core samplers do not disturb the substrate as much as other sampling procedures.[2]

Core samplers have several limitations: (1) core samplers do not work well in sandy or rocky substrates, (2) core samplers collect smaller amounts of sediment and therefore may require additional sampling, and (3) most coring devices are expensive, difficult to handle, and, consequently, have limited use under moderate wave conditions.

There are many different types of core sampling equipment that may be used for sediments. Some require the use of a tripod or truck mounted drill rig operated on a floating plant (barge). Some hand held units can be operated from smaller vessels. Core sampling devices include the split-spoon, the piston-tube or Chicago tube, the vibracore, and hand augers.

The split-spoon sampler is driven by a hammer or weight into the sediment. This method is especially suited for compacted sediments. Good recovery of samples in loose sediments is less dependable. The spoon is typically 2-3 inches in diameter and 2-5 feet long. Successive vertical samples can be taken by driving casing (5 inch pipe) and cleaning out the drill hole between samples.

The piston-tube or Chicago tube sampler is well suited for soft, fine-grained sediments. The sampler is advanced to the starting depth and a tube (typically 3-4 inch diameter) extended hydraulically. Recovery is usually very good since the sample is held in the tube by a partial vacuum. Discrete vertical samples can be obtained without casing.

The vibracore is a long continuous tube that is driven into the sediment using a vibrating action. This method is suited to soft, noncompacted sediments. The entire core is withdrawn and the tube cut into segments for sample extraction. Good recovery with this method requires that the tube penetrate a layer of compacted material, which forms a "cap" at the bottom. The vibration of the tube has been known to consolidate the sample and lose some vertical integrity (a 5-foot drive might produce a 4-foot sample).

Hand augers can be used for sampling very shallow areas or on river banks. Hand operated corers, deployed by a cable from a boat, have been used to collect shallow cores.

3.3.3 Grab Samplers

Grab samplers are less expensive, easier to handle, and often require less manpower than core samplers. Unfortunately, grab samplers cause considerable disruption of

the sediment. Dredge samplers promote loss of the fine-grained fraction of the sediment as well as water soluble compounds and volatile organic compounds (VOCs) which may be present in the sediment. One important criterion for selection of the proper grab sampler is that it consistently collect samples to the required depth below the sediment.

Grab samplers, such as the Ponar and Eckman dredge samplers, are small, lightweight, and can be operated by hand from a small boat. They only collect surface sediments (top 3-6 inches). They have problems with any consolidated (hard packed) deposits. For larger volumes of sample, sometimes needed for treatability tests, a small, commercial clamshell dredge (1-3 cubic yard bucket) can be used.

3.3.4 Other Sampling Considerations

In conjunction with sediment toxicologic assessments, the type and degree of contamination in the interstitial water should be determined. Immediate collection of the interstitial water is recommended since chemical changes may occur even when sediments are stored for a short period of time. Collection of the sediment interstitial water can be accomplished by several methods: centrifugation with filtration, squeezing, suction, and equilibrium dialysis. Each method may alter the original water chemistry. Therefore, decisions about methods for collecting interstitial water should be based on expected contaminants.

Sediment samples should be separated from the collection devices and transported in plastic, polyethylene, or glass containers. Samples that contain volatile compounds should be refrigerated (4° C) or kept on ice to prevent further volatilization. Sediments that are suspected of organic contamination should be transported in brown, borosilicate glass containers with teflon lid liners. Plastic or polycarbonate containers are recommended for metal-bearing sediments. Additional information on sample containers, preservation, storage times, and volume requirements are available in other guidance documents.[3]

3.4 Physical and Chemical Analyses

The type of analysis performed on sediment collected is specific to the purpose and objectives of the plan. There is no "standard" laundry list of analyses which is appropriate to all cases. Some important analyses for consideration are identified in the following paragraphs. Francingues et al[4] provide guidance on testing sediment characteristics.

Physical characteristics often measured are particle size and distribution, organic carbon or volatile matter content, and total solids/specific gravity. Particle size is usefully described by the general size classes of gravel, sand, silt, and clay. Organic carbon should be measured by high temperature combustion rather than chemical oxidation. The latter method does not necessarily fully degrade all carbon classes. Total solids/specific gravity analyses both require a dry sample and are performed in conjunction with each other.[3]

Important chemical analyses include those for pH, oxidation-reduction, salinity conditions, and sulfide content as well as the amount and type of cations and anions, and the amount of potentially reactive iron and manganese. Much can be inferred from the pH and oxidation-reduction conditions when they are analyzed in conjunction with the physical properties.[5] The pH becomes a problem when the dredged material has a pH below 5 or above 8.5 or when it changes during handling and disposal. Whether the sediments are oxidizing or reducing will affect the availability of various contaminants during handling and disposal of the sediments.[6]

3.5 Modeling Sediment Transport and Contaminant Fate and Transport

Sediment transport and contaminant transport and fate models have two applications: (1) they can be used as a screening tool in predicting the environmental and health impacts from contaminant exposure during various remediation actions and (2) they can be used diagnostically to investigate sources of contamination. Current models are limited in their predictive ability to function as a screening tool or crude design model, but are developed to such a degree that they are being applied in this respect for the Buffalo River, New York. Diagnostic modeling is being done for the Sheboygan River, Wisconsin.

Sediment transport models are linked to hydrodynamic models and predict sediment movement due to circulation. Different models have been developed for a variety of sediment environments including lakes, harbors, estuaries, coastal areas, and rivers. The models may be one-, two-, or three-dimensional, depending on the nature of the water body. The one-dimensional models, HYDRO1D-DYNHYD, HYDRO1D-RIVMOD, and HSPF, are used for rivers, streams, and watersheds. The two-dimensional model, HYDRO2D-V, is generally the first choice of the Environmental Research Laboratory (ERL) and has application for estuaries, shallow lakes and bays, and streams. The HYDRO2D-V is being used to model arsenic contamination in New Jersey and is planned for use in Montana mining district streams and in modeling the south bay in San Francisco Bay. The three-dimen-

sional model, HYDRO3D-V, has application for stratified bodies of water, such as lakes, and has been tested in CB studies for Green Bay, Wisconsin. Correct data is important to proper functioning of these models. These models are in different stages of refinement, but all are available from the ERL in Athens, Georgia.[7,8,9]

Fate and transport models mimic the physical and chemical environment of sediments and predict how contaminants and sediments interact, particularly as conditions change. The HYDRO2D-V, also used as a sediment transport model, has been used to model adsorbed contaminants, but does not incorporate other contaminant processes. The WASP4 model is a general purpose, mass balance model incorporating a number of parameters and is considered the state-of-the-art fate and transport model by ERL and a number of EPA offices. The WASP4 has been adopted for toxics management by the Great Lakes National Program Office. Studies using WASP4 focus on Green Bay, Lake Ontario, and Saginaw Bay. The WASP4 also simulates fish and food chain bioaccumulation and is being used to model these in the Buffalo River, New York; the Sheboygan River, Wisconsin; and Saginaw Bay, Michigan.

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